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Electronic spectra of oxadiazoles

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Abstract : MRINDO/S calculation augmented by singly excited configuration interaction was performed on oxadiazoles. Net charge distributions, ionization potentials and electronic spectra of oxadiazoles are reported. The Rydberg transitions are also discussed.

Keywords : Oxadiazoles, ionization potentials, electronic spectra

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1. Introduction

'Azole' is the suffix used for the five membered ring containing two or more heteroatoms, at least one of which is nitrogen. Diazoles are di-aza substituted derivatives of the parent compound furan. There are four oxadiazoles which are derived by the replacement of two ≥ CH groups by the two ≥ N : with varied positions in the ring. The ground state properties of oxadiazoles were studied experimentally as well as theoretically [1] but their excited-state properties were not accounted for. This led us to consider oxadiazoles with a view to account for their ground as well as excited state properties. The ground state properties are compared with experimental and theoretical results cited in Table 1. Because of the lack of theoretical or experimental data for the excited state properties of oxadiazoles we compare our results with those of furan and discuss how the π spectrum of furan is affected by the substitution of two lone-pair atoms.

The optimized geometries of the molecules were taken from various sources [2-4].

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2. Outline of the work

In the MRINDO/S method we added to the basis H2*s*, H2*p*, C3*s*, C3*p*, O3*s*, O3*p*, N3*s* and N3*p* Slater atomic orbitals. These orbitals are called outer (Rydberg) orbitals and the basis set thus formed is called the extended basis set. By the use of such extended basis set one can interpret whether an electronic transition leads to the Rydberg orbital or not. The details of the theoretical methodology can be found in Ref. [5]. This method has been applied with success to account for the electronic spectra of N_2H_2 isomers [6].

3. Results

Table 1 contains ionization potentials deduced from Koopmans theorem [7] and the corresponding orbital symmetries. The experimental values for the ionization potentials are given in the first column whereas the second set of columns give the *ab initio* values for the ionization potentials and the corresponding orbital symmetries. These were taken from NyGaard and Rasmus [1].

Table 2 contains the lowest singlet-singlet transition energies, oscillator strengths, and symmetries of the excited

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Table 1. The lowest ionization potentials of oxadiazoles (eV).

Molecule	Experimental[a]	*ab initio*[a]		MRINDO/S		
(symmetry)	I.P.	I.P.	symmetry of orbital	I.P.	symmetry of orbital	Type
1,2,5-oxadiazole	11.79	12.61		11.11		π
(C_{2v})	11.79	13.22		11.56	v_1	π
	12.00	13.48		11.63	b_2	σ,n
	12.75	14.40		12.41	a_1	σ
	14.40	16.23		13.15		σ, n
	14.40	18.07		15.01		π, n
	16 63	19.55	b_1	15.79		σ
	17.70	21.05	a_1	18.19		σ
	20.78	23.41	b_2	21.94		σ
	21.25	23.82	a_1	22.23		σ
	26.60	32.72	a_1	30.39		σ
		33.72	b_2	30.43		σ
1,3,4-oxadiazole	10.95	11.88		10.35		π
(C_{2v})	11.29	12.44		11.37		σ
	12.30	14.10		11.39		σ,n
	12.70	14.20		12.11		π,n
	15.45	16.88		14.45		σ
	15.45	18.93		15.38		π
	16.35	19.72		15.52		σ
	18.15	21.37		17.43		σ
		23.76		21.69		σ
		24.13		22 40		σ
1,2,3-oxadiazole				10.23	a''	π
(C_s)				11.71	a'	σ, n
				11.99	a''	π, n
				12.22	a'	σ, n
				13.69	a'	σ
				15.19	a''	π, n
				15.85	a'	σ
				18.26	a'	σ
				21.34	a'	σ
				22.62	a'	σ
				26.34	a'	σ
1,2,4-oxadiazole				10.78	a''	π
(C_s)				11.26	a'	σ
				12.06	a''	π, n
				12.43	a'	σ, n
				14.03	a'	σ, n
				14.65	a'	σ
				15.21	a''	π
				17.77	a'	σ
				21.86	a'	σ
				22.45	a'	σ
				29.28	a'	σ

[a] Ref. [1]

states. The first set of columns contain experimental transition energies and oscillator strengths of $\pi \rightarrow \pi^*$ transitions in furan. These were taken from Pickett *et al* [8] to compare our results. The last set of columns of Table 2 contain the percentages Rydberg character of the states. Table 3 gives transition energies, symmetries of the excited states, splittings of the five lowest singlet-triplet transitions, and the percentages Rydberg character of each state.

The results are compared mostly with the experimental and *ab initio* values cited in Table 1 and Table 2 ; otherwise proper references are noted. Transition energies for Rydberg excitations and valence excitations occuring at considerably low wavelengths are not cited in Table 2 and Table 3.

4. Discussion

4.1. Charge distribution :

The net charge distribution in oxadiazoles is shown in Figure 1. According to the general chemical intuition, the higher the positive charge on H in a compound, the higher is its acidic character. So, more easily it may be replaced by metal. The higher the electron density on N, the higher is its donor character. If positive charge is developed on N, its donor character is diminished. On this ground, the H atoms in 1,2,5-oxadiazole seem to be less acidic than those in other oxadiazoles. All the nitrogen atoms in the molecular series except a single nitrogen atom in 1,2,3-oxadiazole exhibit donor character. The carbon atoms show electropositive character throughout the molecular series.

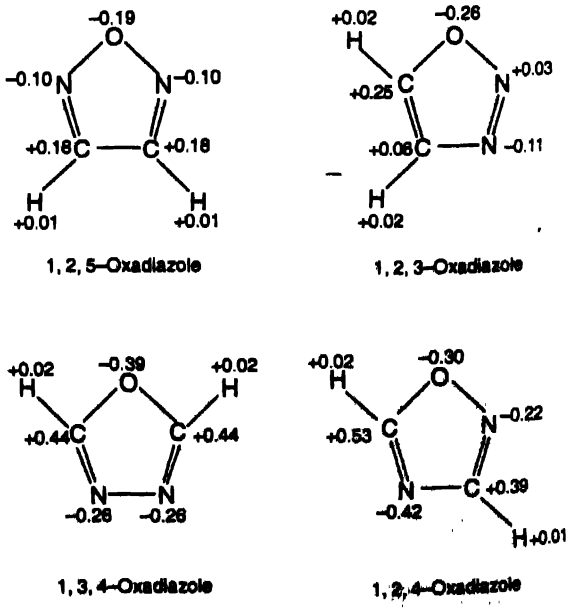

Figure 1. Net charge distribution in oxadiazoles.

Table 2. The lowest singlet-singlet transitions in oxadizoles. All energies are in eV.

Molecule (symmetry)	Experimental[a]		MRINDO/S				% Rydberg Character			
	Transition energy	f	Transition energy	f	Sym. of excited state	Type of transition	H	C	N	Total + 0
1,2,5-oxadiazole	5.9	0.12	3.19	0.000		$n\rightarrow\pi^*$	0	0	0	0
(C_{2v})	6.5	0.08	3.87	0.000		$\sigma\rightarrow\pi^*$	0	0	0	0
	7.4	vs	4.01	0.027		$\pi\rightarrow\pi^*$	0	0	0	0
			4.12	0.027	A_1	$\pi\rightarrow\pi^*$	0	0	0	0
			4.79	0.000	B_1	$\sigma\rightarrow\pi^*$	0	0	0	0
			5.15	0.000	B_1	$\pi\rightarrow\sigma^*$	0	0	0	0
			5.27	0.000	A_1	$\pi\rightarrow\sigma^*$	0	0	0	0
			5.34	0.018		$\pi\rightarrow\pi^*$	0	0	0	0
			5.73	0.000		$\pi\rightarrow\sigma^*$	0	0	0	0
			5.79	0.000		$n\rightarrow\pi^*$	0	0	0	0
			5.90	0.006		$\pi\rightarrow\pi^*$	0	0	0	0
			5.98	0.000		$\pi\rightarrow\sigma^*$	0	0	0	0
			6.11	0.000		$\sigma\rightarrow\pi^*$	0	0	0	0
			6.54	0.053		$\pi\rightarrow\pi^*$	0	0	0	0
			6.75	0.000		$\sigma\rightarrow\pi^*$	0	0	0	0
1,3,4-oxadiazole			3.76	0.000		$n\rightarrow\pi^*$	0	0	0	0
(C_{2v})			3.84	0.000		$\sigma\rightarrow\pi^*$	0	0	0	0
			3.99	0.031		$\pi\rightarrow\pi^*$	0	0	0	0
			4.58	0.022		$\pi\rightarrow\pi^*$	0	0	0	0
			4.59	0.000		$\pi\rightarrow\sigma^*$	0	0	0	0
			4.74	0.000		$n\rightarrow\pi^*$	0	0	0	0
			4.79	0.000		$\sigma\rightarrow\pi^*$	0	0	0	0
			5.04	0.000		$\pi\rightarrow\sigma^*$	0	1	0	1
			5.14	0.006		$n\rightarrow\pi^*$	0	0	0	0
			5.56	0.013		$n\rightarrow\pi^*$	0	0	0	0
			6.03	0.009		$\sigma\rightarrow\sigma^*$	0	0	0	0
			6.17	0.000		$n\rightarrow\sigma^*$	1	1	0	2
			6.37	0.012		$n\rightarrow\sigma^*$	0	0	0	0
			6.80	0.000		$\pi\rightarrow\sigma^*$	1	2	0	3
			6.85	0.059	a_2	$n\rightarrow\sigma^*$	0	0	0	0
1,2,3-oxadiazole			2.90	0.000	A''	$n\rightarrow\pi^*$	0	0	0	0
(C_s)			3.27	0.049	A'	$\pi\rightarrow\pi^*$	0	0	0	0
			3.61	0.000	A''	$n\rightarrow\pi^*$	0	0	0	0
			4.17	0.000	A''	$\pi\rightarrow\sigma^*$	0	0	0	0
			4.38	0.006	A'	$n\rightarrow\pi^*$	0	0	0	0
			5.10	0.000	A''	$\pi\rightarrow\sigma^*$	0	1	0	1
			5.11	0.065	A'	$\pi\rightarrow\pi^*$	0	0	0	0
			5.30	0.000	A''	$n\rightarrow\pi^*$	0	0	0	0
			5.42	0.000	A''	$\sigma\rightarrow\pi^*$	0	0	0	0
			5.88	0.004	A'	$n\rightarrow\sigma^*$	0	0	0	0
			5.92	0.000	A''	$\pi\rightarrow\sigma^*$	1	2	1	4
			6.28	0.000	A''	$\sigma\rightarrow\pi^*$	0	0	0	0
			6.48	0.057	A'	$n\rightarrow\pi^*$	0	0	0	0
			6.62	0.000	A'	$n\rightarrow\sigma^*$	3	10	3	16
			6.71	0.026	A'	$n\rightarrow\sigma^*$	0	0	0	0

4.2. Ionization potentials :

The *ab initio* calculations [1] predict the following configurations for 1,2,5- and 1,3,4-oxadiazoles.

1, 2, 5-oxadiazole : $a_2\, b_1\, b_2\, a_1\, a_1\, b_2\, b_1\, a_1\, b_2\, a_1\, a_1\, b_2$

1,3,4- oxadiazole : $a_2\, b_2\, b_1\, a_1\, a_1\, b_2\, b_1\, a_1\, a_1\, b_2$

Each of these orbitals is filled with two electrons. The present calculation predicts these configurations as follows :

1, 2, 5-oxadiazole : $a_2\, b_1\, b_2\, a_1\, a_1\, b_1\, b_2\, a_1\, b_2\, a_1\, b_2\, a_1$

1,3,4- oxadiazole : $a_2\, b_2\, a_1\, b_1\, a_1\, b_1\, b_2\, a_1\, b_2\, a_1$

It is evident therefore that the present configurations are in reasonable agreement with the *ab initio* calculations.

The highest occupied MO of oxadiazoles is assigned as an out-of-plane π orbital. This is consistent with the *ab initio* calculation for 1,2,5- and 1,3,4-oxadiazoles. In addition, the computed ionization potentials of 1,2,5- and 1,3,4-oxadiazoles are in close agreement with the experimental values whereas the *ab initio* values show large deviation. In this context, our calculation seems to be better than the *ab initio* one. On this ground, the computed ionization potentials of 1,2,3-oxadiazole and 1,2,4-oxadiazole may be expected to be correct.

4.3. Singlet excitations :

The singlet excitations of oxadiazoles have not been observed or calculated. The electronic spectrum of their parent compound furan has been observed and critically analysed [8-12]. The ultraviolet spectrum of furan has been reported by Pickett *et al* [8] and Watanabe and Nakayama [9]. Since then there has been several attempts to interpret the spectrum of furan

Table 2. Contd..

Molecule (symmetry)	Experimental[a]		Mrindo/s				% Rydberg Character			
	Transition energy	f	Transition energy	f	Sym. of excited state	Type of transition	H + 0	C	N	Total
1,2,4-oxadiazole			3.50	0.000	A''	$n \rightarrow \pi^*$	0	0	0	0
(C_s)			4.02	0.000	A''	$n \rightarrow \pi^*$	0	0	0	0
			4.16	0.029	A'	$\pi \rightarrow \pi^*$	0	0	0	0
			4.64	0.001	A'	$n \rightarrow \pi^*$	0	0	0	0
			4.82	0.000	A''	$\pi \rightarrow \sigma^*$	1	5	1	7
			5.00	0.031	A'	$\pi \rightarrow \pi^*$	0	0	0	0
			5.16	0.000	A''	$n \rightarrow \pi^*$	0	0	0	0
			5.46	0.000	A''	$\pi \rightarrow \sigma^*$	0	0	0	0
			5.89	0.000	A''	$n \rightarrow \sigma^*$	1	3	0	4
			5.99	0.029	A'	$n \rightarrow \pi^*$	0	0	0	0
			6.03	0 000	A''	$n \rightarrow \pi^*$	0	0	0	0
			6.22	0.072	A'	$n \rightarrow \sigma^*$	0	0	0	0
			6.53	0.000	A''	$n \rightarrow \pi^*$	0	1	0	1
			6.66	0.004	A'	$n \rightarrow \sigma^*$	1	6	1	8
			6.76	0 000	A''	$\sigma \rightarrow \pi^*$	0	0	0	0

[a] Ref. [8]

Table 3. The five lowest singlet-triplet transitions in oxadiazoles. All energies are in eV.

Molecule (symmetry)	MRINDO/S			
	Transition energy	S-T split	Symmetry of excited state	Type
1,2,5-oxadiazole	1.62	2.39	B_2	$\pi \rightarrow \pi^*$
(C_{2v})	2.20	1.92	A_1	$\pi \rightarrow \pi^*$
	2.48	0.71	A_2	$n \rightarrow \pi^*$
	3.13	0.74	B_1	$\sigma \rightarrow \pi^*$
	4.09	1.25	A_1	$\pi \rightarrow \pi^*$
1,2,4-oxadiazole	1.90	2.68	A_1	$\pi \rightarrow \pi^*$
(C_{2v})	1.92	2.07	B_2	$\pi \rightarrow \pi^*$
	3.13	0.69	B_1	$n \rightarrow \pi^*$
	3.17	0.67	A_2	$\sigma \rightarrow \pi^*$
	3.99	0.60	A_2	$\pi \rightarrow \sigma^*$
1,2,3-oxadiazole	0.95	2.32	A'	$\pi \rightarrow \pi^*$
(C_s)	2.21	0.69	A''	$n \rightarrow \pi^*$
	2.34	2.77	A'	$\pi \rightarrow \pi^*$
	2.86	0.75	A''	$n \rightarrow \pi^*$
	3.11	1.27	A'	$n \rightarrow \pi^*$
1,2,4-oxadiazole	2.26	1.90	A'	$\pi \rightarrow \pi^*$
(C_s)	2.77	2.23	A'	$\pi \rightarrow \pi^*$
	3.10	0.40	A''	$n \rightarrow \pi^*$
	3.41	0.61	A''	$n \rightarrow \pi^*$
	4.19	0.45	A'	$n \rightarrow \pi^*$

theoretically [10-12]. The calculations gave four singlet $\pi \rightarrow \pi^*$ transitions. Horvath and Kiss [13] observed that the furan spectrum consists of at least two $\pi \rightarrow \pi^*$ bands, followed by $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ bands. The π spectrum of furan can be summarised as follows.

Observed : 5.9eV(0.12), 6.5 eV (0.08) and 7.4 eV (very strong).

Calculated : 5.2eV (0.078), 5.8eV (0.009), 7.3eV (0.368) and 7.8 eV (0.097).

The quantities within brackets represent oscillator strengths. The observed values were taken from Pickett *et al* [8] while the calculated values were taken from Del Bene and Jaffe [12]. These observed values are also cited in Table 2.

Derrick *et al* [14] claimed two Rydberg series in furan converging upon the first ionization potential at 73630 cm^{-1} (~ 8.9eV) with $\delta = 0.55$ and $\delta = 0.04$, and a third series with $\delta = 0.82$ converging upon the second ionization potential at 83120 cm^{-1} (~ 10.3 eV). The photoelectron studies of furan [15] indicate that the third Rydberg series has strong structural features and consists of allowed transitions.

(i) *1, 2,5-oxadiazole :* The lowest singlet transition at 3.19 eV is a forbidden $n \rightarrow \pi^*$ transition. However, the $n \rightarrow \pi^*$ transition at 7.8eV is an allowed one since it has an oscillator strength of 0.033. The overall symmetry of the state is A_1. This is consistent with the furan spectrum in which Del Bene and Jaffe [12] predicted that the $n \rightarrow \pi^*$ transition occurs at considerably low wavelength, far in the vacuum ultraviolet. We report five $n \rightarrow \pi^*$ transitions in 1,2,5-oxadiazole among those are the two at 4.01 and 4.12 eV equally intense (f = 0.027). The other three at 5.34eV (0.018), 5.90 eV (0.006) and 6.54eV (0.053) can be compared with the observed $\pi \rightarrow \pi^*$ transitions in furan [8]. The quantities within brackets represent oscillator strengths. The most intense (f = 0.350) transition in 1,2,5-oxadiazole is assigned as a $\sigma \rightarrow \sigma^*$ transition at 8.54eV. Thus, this energy corresponds to the maximum absorption in 1,2,5-oxadiazole.

The spectrum of 1,2,5-oxadiazole consists of two Rydberg series converging upon the first ionization potential at 11.11eV. The first series consists of only one member at 8.9 eV with $\delta = 0.88$ and hence this series corresponds to *ns* Rydberg series. The second series consisting of two members at 8.57 and 8.72eV with $\delta = 0.69$ and $\delta = 0.62$ corresponds to *np* Rydberg series. The only Rydberg transition at 8.72eV exhibits intensity (f = 0.001). Thus, we find the Rydberg spectrum of 1,2,5-

Oxadiazole to look like that of furan [15]. It is worthwhile to notice that this Rydberg transition lies in the vicinity of the most intense transition and hence its observation would be difficult in the absence of special experimental condition.

(ii) 1,3,4-oxadiazole : The spectrum of 1,3,4-oxadiazole consists of two allowed $n \rightarrow \pi^*$ transitions. These transitions appear to come at 5.14 and 5.56eV, the former being less intense ($f = 0.006$) than the latter ($f = 0.013$). We report four $\pi \rightarrow \pi^*$ transitions in 1,3,4-oxadiazole. This is in accord with the π spectrum of furan as calculated by Del Bene and Jaffe [12]. These transitions in 1,3,4-oxadiazole are calculated at 3.99 eV (0.031), 4.58eV (0.022), 8.21eV (0.225) and 8.88eV (0.382) ; the quantities within brackets represent oscillator strengths. It is worthwhile to notice that the most intense transition in 1,3,4-oxadiazole is the $\pi \rightarrow \pi^*$ transition at 8.88eV. Thus, this energy corresponds to the maximum absorption in 1,3,4-oxadiazole.

The spectrum of 1,3,4-oxadiazole comprises two Rydberg series converging upon the first ionization potential at 10.35eV. The first series consists of only one member at 7.44eV with $\delta = 0.84$ and hence corresponds to *ns* Rydberg series. The second series corresponds to *np* Rydberg series. This series consists of five members at 8.32eV (0.62), 8.50eV (0.30), 8.54eV (0.26), 8.55eV (0.25) and 8.62eV (0.20) ; the quantities within brackets represent quantum defects. For the molecules built up from atoms of the first period, δ is small (≤ 0.1) for states derived from nd electrons and somewhat larger (0.3–0.5) for np electrons. The quantum defects of the last three members of *np* Rydberg series are less than 0.3 but the analysis of antibonding orbitals does indicate that the electrons are mostly populated on the 3*p* atomic orbitals of carbon, oxygen and nitrogen atoms. Thus, we call them the members of np Rydberg series. Only these members exhibit intensity but these are two weak as compared with the most intense band of the spectrum (at 8.88eV with $f = 0.382$).

(iii) 1,2,3-oxadiazole : The spectrum of 1,2,3-oxadiazole consists of three allowed $n \rightarrow \pi^*$ transitions. These transitions come at 4.38, 6.48 and 7.07eV with respective oscillator strengths of 0.006, 0.057 and 0.021. It is worthwhile to notice that the spectrum of 1,2,3-oxadiazole consists of only two $\pi \rightarrow \pi^*$ transitions. These transitions are calculated at 3.27 and 5.11eV, the former being less intense ($f = 0.049$) than the latter ($f = 0.065$). Thus the π spectrum of furan seems to be lost to some extent in 1,2,3-oxadiazole. The maximum absorption in 1,2,3-oxadiazole occurs at about 9.08eV. The band associated with the maximum absorption is assigned as a $\sigma \rightarrow \sigma^*$ transition with $f = 0.697$.

We report *ns* and *np* Rydberg series in 1,2,3-oxadiazole. The *ns* Rydberg series converges upon the first ionization potential (10.23eV) and consists of only one member at 7.22eV with $\delta = 0.87$. The *np* Rydberg series consists of six members. The first five memebrs of this series converge upon the first ionization potential, while the last member at 9.49eV with $\delta = 0.52$ converges upon the second ionization potential (11.71eV). The members converging upon the first ionization potential come at 7.99eV (0.64), 8.14eV (0.45), 8.24eV (0.28), 8.36eV (0.31) and 8.44eV (0.25); the quantities within brackets represent quantum defects. Thus the Rydberg spectrum of 1,2,3-oxadiazole differs from those of 1,2,5-oxadiazole and 1,3,4-oxadiazole. The only Rydberg transition at 8.36eV exhibits intensity ($f = 0.016$) and lies very close to the most intense transition (at 9.08eV).

(iv) 1,2,4-oxadiazole : The spectrum of 1,2,4-oxadiazole consists of two $\pi \rightarrow \pi^*$ transitions. These transitions are calculated at 4.15 and 5.00eV, the former being less intense ($f = 0.029$) than the latter ($f = 0.031$). Thus, the π spectrum of 1,2,4-oxadiazole looks much like that of 1,2,3-oxadiazole. We report two allowed $n \rightarrow \pi^*$ transitions in 1,2,4-oxadiazole to come at 4.64 and 5.99eV, the former being less intense ($f = 0.001$) than the latter ($f = 0.029$). The most intense transition in 1,2,4-oxadiazole is assigned as a $\sigma \rightarrow \sigma^*$ transition at 8.97eV which has an oscillator strength amounting to 0.315.

Contrary to the other oxadiazoles, we report *ns*, *np* and *nd* Rydberg series in 1,2,4-oxadiazole. These series converge upon the first ionization potential at 10.78eV. The *ns* Rydberg series consists of only one member at 7.86 eV with $\delta = 0.84$. The *np* Rydberg series consists of two members at 8.29 and 8.82eV with $\delta = 0.66$ and $\delta = 0.34$. The *nd* Rydberg series also comprises two members at 8.97 and 9.21 eV with $\delta = 0.1$ and $\delta = 0.05$. The only Rydberg transition at 8.29eV and at 9.21eV exhibit intensity, the former being less intense ($f = 0.003$) than the latter ($f = 0.003$). It is worthwhile to notice that these Rydberg transitions lie near the region of maximum absorption.

4.4. Triplet excitations :

The experimental benchmarks of the calculations are the separations between the lowest singlet $\pi - \pi$ and $n - \pi$ states, the separations between the lowest singlet and triplet $n - \pi$ states and the intensities of $n \rightarrow \pi^*$ transitions. As discussed earlier, the $n \rightarrow \pi^*$ transitions in oxadiazoles exhibit intensity. The separations between the lowest singlet $\pi - \pi$ and $n - \pi$ states are 0.82eV in 1,2,5-oxadiazole, 0.23eV in 1,3,4-oxadiazole, 0.37eV in 1,2,3-oxadiazole, and 0.66eV in 1,2,4-oxadiazole. The separations between the lowest singlet and triplet $n - \pi$ states are 0.71, 0.63, 0.69 and 0.40eV in 1,2,5-, 1,3,4-, 1,2,3-, and 1,2,4-oxadiazole, respectively.

5. Conclusion

The replacement of CH in furan by $\geq N$: removes CH bonding level and introduces a lone-pair level which is characterised by very high coefficients of $2S_N$ and $2P_N$ in the molecular orbital. The spectrum of each species consists of the least one allowed Rydberg transition with small intensity. These less intense Rydberg transitions in oxadiazoles lie in the vicinity of their respective maximum absorption bands and hence, they may be observed with special experimental conditions. The calculation reveals that the substituent shifts the frequencies of the furan bands and alters their intensities somewhat. Thus, furan shows a lot of resistance to change its π spectrum.

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References

[1] L NyOaard and L H Rasmus *J. Mol. Struct.* **12** 59 (1942)

[2] A R Katritzky *Hand Book of Heterocyclic Chemistry* (New York : Pergaman) p93 (1965)

[3] MH Palmer and R H Findlay *J. Mol. Struct.* **40** 191 (1972)

[4] M Roche, FD Amato and M Benard *J. Mol. Struct.* **9** 183 (1971)

[5] R S Prasad and B N Rai *Theor. Chim. Acta* **77** 343 (1990)

[6] R S Prasad and A K Singh *Indian J. Phys.* **76B** 171 (2002)

[7] T Koopmans *Physica* **1** 104 (1933)

[8] L Pickett, N J Hoeffich and T C Lui *J. Am. Chem. Soc.* **73** 4862 (1951)

[9] K Watanabe and T Nakayama *J. Chem. Phys.* **29** 48 (1958)

[10] M K Orloff and D D Pitds *J. Chem. Phys.* **38** 2334 (1963)

[11] L Pajol and A Jug *Theor. Chim. Acta* **2** 133 (1964)

[12] J Del Bene and H H Jaffe *J. Chem. Phys.* **48** 4050 (1968)

[13] G Horvath and A I Kiss *Spectro. Chim. Acta* **23A** 921 (1967)

[14] P J Derrick, L Asbrink, O Edqvist, B O Jonsson and E Lindholm *Int. J. Mass Spectrom. Ion. Phys.* **6** 161 (1971)

[15] J H D Eland *Int. J. Mass Spectrom. Ion Phys.* **2** 471 (1969)